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16. ABSTRACT

A review of EPA's Quality Assurance Program for monitoring NO_2 in ambient air is presented. Included are a discussion of the nationwide audit program, special audits of continuous monitors, the preparation of NO_2 audit samples and a general interpretation of the results of these programs.

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CHAPTER 7

REVIEW OF U.S. ENVIRONMENTAL PROTECTION AGENCY NO_2 MONITORING QUALITY ASSURANCE PROGRAM

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INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has an active program to upgrade the quality of air pollution monitoring data collected in the United States. Regulated pollutants of the ambient air and in source emissions receive the major emphasis of the program. This quality assurance program for air pollution measurements is divided into two major subprograms. The first subprogram evaluates the methodology used for measuring regulated pollutants to determine if it can make the required measurements. A part of this subprogram corrects defects in measurement methodology whenever they are identified. The subprogram on methodology evaluation is discussed in Chapter 4 and elsewhere [1].

The other part of the program evaluates the performance of control agencies required to monitor for air pollutants in support of regulations and of monitoring projects that make air pollution measurements important to EPA for various reasons. Performance evaluation is determined using samples of materials that contain the appropriate pollutants in known amounts at several concentration levels. These samples are submitted in a blind fashion to the organization under evaluation, which then analyzes the samples; their

results are compared with the true values for the samples. The term performance audit is used to describe this activity. A discussion of the EPA program for evaluating the performance of a variety of organizations that measure nitrogen dioxide (NO_2) follows.

AUDIT SAMPLES

Nitrogen dioxide, as is the case with a number of gaseous pollutants, can be measured on a time-integrated basis or as a continuous measurement. For each type of measurement, the most satisfactory audit sample would be an atmosphere containing known amounts of gaseous NO_2, whose concentration could be varied to cover the concentration range most likely to be encountered. For analyzers that measure NO_2 continuously, atmospheres of NO_2 are the only feasible audit samples. Time-integrated measurement methods generally collect ambient NO_2 in an absorbing reagent, and appropriate solutions can be used as audit samples.

NO_2 Atmosphere Audit Samples

Preparing and using an atmosphere containing subpart per million levels of NO_2 presents special problems. Compressed gaseous mixtures in cylinders have been used successfully, but the slow change in NO_2 concentration in these mixtures requires frequent analysis to be certain of the NO_2 concentration at the time of audit. Another method to obtain audit atmospheres of NO_2 takes advantage of the rapid and quantitative gas-phase reaction of nitric oxide (NO) with ozone (O_3) to produce NO_2, as shown in Equation 1 [2]:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

In practice, atmospheres containing known amounts of NO_2 are continuously generated in a dynamic system, in which a gas stream containing a known concentration of NO is mixed with O_3 to give an atmosphere containing known concentrations of NO_2. This atmosphere is then used to audit a continuous NO_2 analyzer.

This procedure, known as gas-phase titration, requires a rather skilled operator and specialized equipment. For these reasons, gas-phase titration, as a basis for auditing NO_2 analyzers, is used only in special monitoring programs where the expense is justified. Prototype devices that can be shipped easily from point to point and simply operated are presently being evaluated for possible use in nationwide audits of control agencies using continuous NO_2 analyzers.

NO_2 Solution Audit Samples

For time-integrated samples, NO_2 is generally collected by passing a measured amount of ambient air through a solution that selectively removes the NO_2 and converts it to nitrite ion. The concentration of nitrite ion is

determined by conventional conversion to an azo dye and colorimetric determination. Aqueous solutions of sodium nitrite are convenient audit samples for the analytical portion of time-integrated measurements of ambient NO_2.

AUDITS OF NO_2 MEASUREMENTS

Nationwide Audits of Time-Integrated Measurements

Introduction

Since 1972, EPA has conducted a performance audit program of the various monitoring groups throughout the United States and several foreign countries. Auditing the analytical performance of the measurement of NO_2 by time-integrated methodology has been a part of this program. The performance audit program is one part of an overall quality assurance program for NO_2 measurements, and the results can give quite meaningful information on the overall quality of NO_2 measurements.

The most important purpose of the performance audit program is to provide a monitoring organization a means to rapidly evaluate their analyses themselves. Performance in the analysis of audit samples when the concentrations are unknown to the analyst is a very useful means of identifying problems and determining the corrective action needed. Rapid self-evaluation and correction of errors is one of the fundamental precepts of EPA's quality assurance program. The results of the performance audit program also provide EPA with the continuing index of the validity of monitoring data used in making important decisions.

Program Coordination

Participants are selected by the Regional Quality Control Coordinators in each of EPA's ten regions throughout the United States. Additional participants are obtained through individual request and through notification in the *Journal of the Air Pollution Control Association*.

After the audit roster is completed for a particular survey, instructional materials and audit samples are mailed to participants, who are allowed 5–6 weeks to analyze the samples and return their results. The results are entered into a computerized data handling system, which calculates statistics. Individual reports are returned to participants showing the acceptable ranges for each sample as well as the values they reported.

To determine whether an incorrect result is due to inherent problems in the laboratory procedure or whether the error is a one-time phenomenon, recheck samples are sent to laboratories whose results do not meet certain criteria. Thus, by having a second chance to analyze a set of samples, real deficiencies are distinguished from one-time problems.

Statistical Approach

Acceptance criteria, which can be used to judge the performance of participants, are an important, yet vexing, requirement of the program. The program has developed acceptance criteria that the participants themselves can use to judge their own performance. The criteria must be used with judgment because it is unlikely that any one set of criteria can serve the needs of all data users. The system used in this program was developed from the results of analyses by experienced laboratories, by the variability in results caused by the samples themselves and by the variability expected between laboratories during a survey.

Two acceptable ranges have been defined. The Sample Range contains the variability attributable to the sample material. In each survey, this range is based on the results of repeated analyses of several samples from each concentration range by one laboratory. These ranges are goals for each participant. It is not reasonable to expect all participants to fall within these ranges on any given analysis. However, falling within these ranges repeatedly indicates a laboratory with excellent precision and accuracy in the analysis for NO_2. Falling outside the sample range does not indicate a problem.

A second acceptable range, the Target Range, has been constructed to include between-laboratory variability as well as sample variability. A participant falling outside the sample range but within the Target Range should feel comfortable with his results. If, however, the results fall outside the Target Range, the accuracy of the analysis should be suspect. The Target Range is based in part on past performance of all participants. For a particular survey, an average percentage difference between the reported and true results for all past surveys is determined and used to calculate the Target Range for a survey.

The method of evaluating the results of a survey is under review, and changes are likely in the means of judging performance.

Results

Results from four performance audits during 1976 and 1977 are presented to show the type of information this program produces [3,4]. Nitrogen dioxide audit number 0676 began in June 1976: out of 119 sample sets requested by participants, 100 sets of data were returned for a response rate of 84%. This and corresponding information for audits begun in December 1976, June 1977 and December 1977, are shown in Table I. Table I also indicates the monitoring agency-type distribution.

Methods used to analyze samples can be grouped into five broad categories, as defined by the participants. Table II lists the analytical methods used and the number of participants using the method. Participants tend to define the analytical method used in very general terms. A laboratory reporting the use of the manual sodium arsenite procedure as the method of choice may have used that procedure with various modifications. Thus, Table II should be interpreted to indicate the number of laboratories that used the procedure of approximating the method specified in the Table.

Table I. NO_2 Agency Distribution

	Foreign	EPA	State	Local	Private	Total	% Return
NO_2 Audit–0676							
Agencies Requesting Samples	2	10	45	55	7	119	
Agencies Returning Data	2	8	38	50	2	100	84.0
NO_2 Audit–1276							
Agencies Requesting Samples	2	11	47	57	13	130	
Agencies Returning Data	1	8	41	50	10	110	84.6
NO_2 Audit–0677							
Agencies Requesting Samples	1	9	41	60	12	123	
Agencies Returning Data	1	6	37	44	7	95	77.2
NO_2 Audit–1277							
Agencies Requesting Samples	1	9	41	58	15	124	
Agencies Returning Data	1	5	37	40	7	90	72.6

AVERAGE: 79.6%

Table II. NO_2 Analytical Methods

Method	Number Agencies Using Method			
	Audit 0676	Audit 1276	Audit 0677	Audit 1277
Saltzman–Manual	5	3	4	4
Sodium Arsenite–Manual	65	72	62	56
Sodium Arsenite–Automatic	24	28	23	24
TGS–ANSA–Manual	1	3	2	2
Other	4	4	4	4

Table III. NO_2 Sample and Target Ranges (%)

	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5
Sample Range	±10	±10	±10	±10	±10
Target Range	±20	±20	±20	±20	±20

Acceptable Range. As described above, two performance ranges were used as one means of judging performance. The Sample Ranges and Target Ranges for NO_2 in the five concentration ranges used in these audits are shown in Table III in the order of increasing concentration. The percentages given are the allowable differences from true values. Because only a few audits had been conducted previous to the one reported here, considerable judgment has been used in constructing the limits shown in Table III. As more audits are conducted and more data become available, the ranges will be refined.

Data Summary. Using the Target Ranges as one means of eliminating non-representative data, the arbitrary decision was made that any laboratory not reporting at least one value within the Target Ranges would be considered an outlier. The Target Ranges are sufficiently broad that unless the analyses are totally out of control, at least one value would fall within the ranges of the laboratory's performance similar to most of the study population. The remainder of this chapter deals with all reported results except those values identified as outliers using the above test.

Table IV is a frequency distribution of the percent differences between the reported value and the true value for each sample concentration for each audit. Table IV is very useful for laboratories trying to determine their performance relative to other participants. For example, in the 1276 audit, only 10% of the laboratories reporting results for concentration 1 had a percent difference of 0.8% or less, while 50% of the laboratories reported a percent

Table IV. NO_2 Absolute Percent Difference

	No.	Minimum	10%	30%	50%	70%	90%	Maximum	Mean
NO_2 Audit–0676									
Conc. 1	91	0.40	1.2	4.8	8.7	12.7	28.2	78.2	12.7
Conc. 2	92	0.00	0.5	1.7	2.4	4.8	11.4	287.4	7.8
Conc. 3	91	0.00	1.0	1.7	3.2	5.1	11.4	104.8	6.2
Conc. 4	91	0.12	0.6	1.6	2.5	4.4	8.4	45.3	4.5
Conc. 5	90	0.10	0.5	1.6	2.4	4.4	15.3	86.4	6.7
All Samples	455	0.00	0.7	1.7	3.2	6.5	15.1	287.4	7.7
NO_2 Audit–1276									
Conc. 1	106	0.0	0.8	5.0	8.3	16.7	30.8	80.0	15.3
Conc. 2	105	0.6	0.6	5.0	8.8	11.6	22.6	81.8	11.4
Conc. 3	108	0.0	0.9	2.4	4.9	7.4	16.6	32.2	7.1
Conc. 4	108	0.2	0.8	3.0	6.0	8.2	14.2	40.5	7.3
Conc. 5	107	0.0	0.5	1.7	3.0	6.3	13.8	34.1	5.4
All Samples	534	0.0	0.8	2.8	6.1	10.1	22.5	81.8	9.3
NO_2 Audit–0677									
Conc. 1	88	0.0	0.8	5.9	9.2	14.3	24.4	77.3	12.7
Conc. 2	91	0.0	0.8	3.4	5.5	9.2	16.4	82.4	8.5
Conc. 3	86	0.4	1.2	2.5	4.9	7.8	17.2	76.2	7.8
Conc. 4	92	0.0	0.5	2.1	3.4	6.9	15.1	74.9	7.8
Conc. 5	90	0.0	0.4	2.0	3.8	5.9	12.2	75.7	5.8
All Samples	448	0.0	0.8	2.9	5.0	9.2	17.6	82.4	8.5
NO_2 Audit–1277									
Conc. 1	84	0.0	0.6	2.2	5.0	7.7	22.1	58.6	9.0
Conc. 2	86	0.3	1.3	3.5	4.5	7.4	15.8	35.7	7.1
Conc. 3	87	0.2	1.8	3.4	4.8	6.8	12.5	19.4	6.0
Conc. 4	86	0.0	1.0	2.2	3.4	5.4	11.9	20.6	5.0
Conc. 5	88	0.1	0.9	1.8	3.1	5.2	9.2	96.1	5.3
All Samples	431	0.0	1.0	2.6	4.2	6.6	13.7	96.1	6.5

difference of 8.3% or less for the same concentration. The mean percent difference for "All Samples" is a most useful statistic for comparing one audit with another. Thus, Table IV shows that this value ranges from 6.5% in audit 1277 to 9.3% in audit 1276; there seems to be no pronounced trend. This discovery indicates that the level of performance in the analysis of NO_2 is stable and that in general, accuracy of about 8–10% can be expected. However, there is a dependence on concentration levels, which must be carefully considered.

Analytical Method Summary. Table V was developed to determine if a particular analytical method produces unduly imprecise or biased results. The results show that all methods estimate true values quite adequately and that no unusually large imprecision is present.

Table V. Mean and Standard Deviation of

Method	Concentration 1		Concentration 2	
	Mean	Standard Deviation	Mean	Standard Deviation
				NO_2 Audit
Saltzman–Manual	0.214	0.045	0.411	0.007
Sodium Arsenite–Manual	0.236	0.040	0.426	0.157
Sodium Arsenite–Automatic	0.228	0.028	0.405	0.017
TGS–ANSA–Manual				
Other	0.228	0.121	0.423	0.033
True Value		0.25		0.41
				NO_2 Audit
Saltzman–Manual	0.11	0.02	0.16	0.03
Sodium Arsenite–Manual	0.12	0.03	0.17	0.04
Sodium Arsenite–Automatic	0.12	0.02	0.16	0.05
TGS–ANSA–Manual	0.14	0.06	0.21	0.04
Other	0.12	0.01	0.17	0.01
True Value		0.12		0.18
				NO_2 Audit
Saltzman–Manual	0.13	0.00	0.25	0.00
Sodium Arsenite–Manual	0.12	0.02	0.25	0.04
Sodium Arsenite–Automatic	0.13	0.01	0.24	0.02
TGS–ANSA–Manual	0.15	0.02	0.26	0.02
Other	0.12	0.02	0.26	0.02
True Value		0.12		0.24
				NO_2 Audit
Saltzman–Manual	0.19	0.02	0.33	0.02
Sodium Arsenite–Manual	0.19	0.03	0.32	0.03
Sodium Arsenite–Automatic	0.18	0.01	0.32	0.01
TGS–ANSA–Manual	0.20	0.00	0.32	0.02
Other	0.22	0.03	0.34	0.02
True Value		0.18		0.31

Special Audits of Continuous Measurements

There are monitoring programs that measure NO_2 continuously and are of enough importance to justify periodic audits of the performance of the analyzers. Portable devices that can generate atmospheres of NO_2 using

NO_2 Results by Analytical Method (μg/ml)

Concentration 3		Concentration 4		Concentration 5	
Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
−0676					
0.408	0.014	0.807	0.033	1.00	0.033
0.415	0.066	0.828	0.076	1.01	0.181
0.403	0.017	0.810	0.032	1.00	0.064
0.425	0.041	0.810	0.023	0.96	0.075
	0.41		0.83		1.02
−1276					
0.34	0.01	0.49	0.04	0.81	0.05
0.32	0.04	0.51	0.06	0.85	0.08
0.32	0.02	0.52	0.03	0.86	0.04
0.35	0.05	0.54	0.04	0.89	0.04
0.31	0.01	0.54	0.01	0.86	0.01
	0.33		0.54		0.87
−0677					
0.25	0.00	0.38	0.00	0.68	0.02
0.25	0.04	0.39	0.06	0.73	0.08
0.24	0.02	0.38	0.03	0.70	0.06
0.25	0.02	0.52	0.19	0.69	0.01
0.26	0.01	0.40	0.04	0.72	0.02
	0.24		0.38		0.69
−1277					
0.52	0.04	0.52	0.02	0.87	0.04
0.52	0.03	0.52	0.03	0.89	0.05
0.52	0.02	0.52	0.02	0.84	0.18
0.52	0.01	0.52	0.00	0.89	0.02
0.53	0.03	0.53	0.03	0.91	0.04
	0.52		0.50		0.87

gas-phase titration are used for these special audits. Because of the complexity of the equipment, a team is required at the monitoring site to perform the audit. All field gas-phase titration audit devices are compared with a laboratory standard apparatus, which is never used for field work. These comparisons are made before and after each audit to ensure that the audit device in fact delivered known NO_2 concentrations.

To conduct this audit, normal monitoring is temporarily interrupted and atmospheres of NO_2 at zero and several upscale levels, generally five or six, are produced by the gas-phase titration apparatus. The monitoring instrument is challenged at each concentration level, and the value indicated by the analyzer is recorded. Statistical analysis of the audit concentrations and analyzer responses is then made to determine how well the analyzer was performing at the time of the audit.

Determination of Performance

Linear regression analysis is used to determine the slope and intercept of the plot of analyzer response vs audit concentration. Perfect agreement between analyzer response and audit concentration would result in a straight line with unity slope and zero intercept. The slope of the line is the measure used to determine overall analytical accuracy, provided the intercept is small compared to the concentrations being analyzed.

Criteria for acceptable performance, as a result of these audits, can only be made in some arbitrary fashion. Each monitoring program is unique, and the requirements, with respect to data quality, differ from one to another. However, there is now enough experience to show that differences of more than 15% between the slope and unity indicate problems, and some corrective action should be taken. Likewise, close agreement between the slope and unity indicates good to excellent performance, and the following arbitrary criteria are used to describe the results of these audits:

- excellent–slope of the regression of analyzer response on audit concentration is $0.95 \leq \text{slope} \leq 1.05$;
- satisfactory–slope of the regression of analyzer response on audit concentration is $0.85 \leq \text{slope} < 0.95$ or $1.05 < \text{slope} \leq 1.115$; and
- unsatisfactory–slope of the regression of analyzer response on audit concentration is slope <0.85 or slope >1.15.

RESULTS

Field performance audits for NO_2 analyzers in a number of important monitoring projects have been conducted and the results reported to the respective program managers for these projects. The results from one project will be given in some detail to show that an audit program does have an impact on improving data quality.

EPA is concerned about the impact on the environment of present and proposed energy developments. The impact on air quality is one of the

major concerns with respect to these energy developments, and many air quality monitoring data are being gathered to determine this impact. It is very important that air quality data obtained from diverse monitoring programs be comparable, and a large-scale quality assurance program has been established for this purpose. The program is being conducted for EPA under

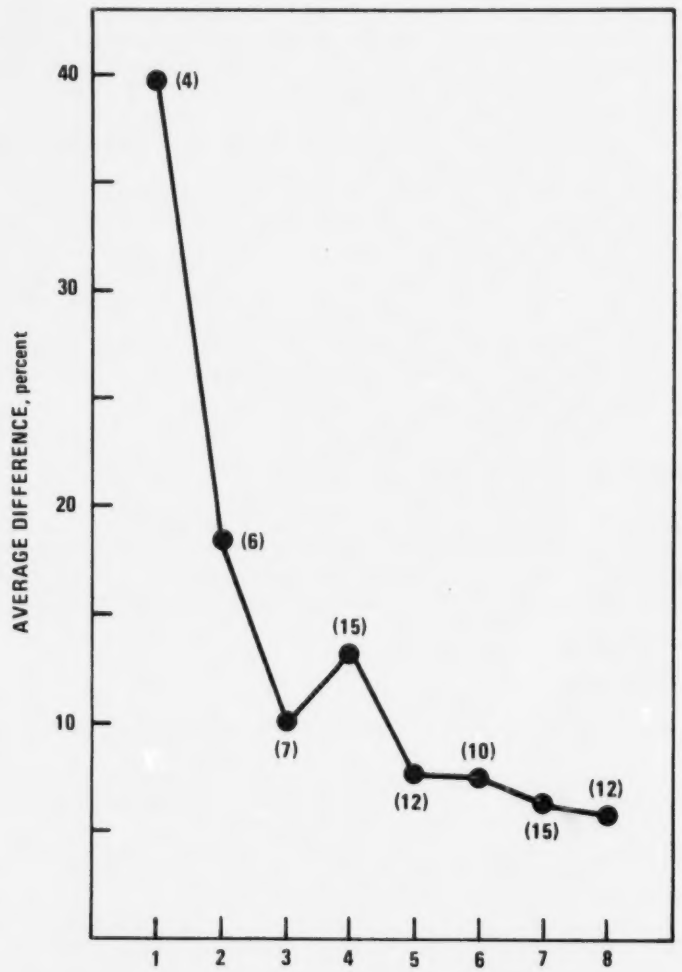

Figure 1. Plot of average difference between slopes and unity for each agency vs the quarterly audit.

contract by the Environmental Monitoring and Services Center of Rockwell International.

Up to this point, the program has been concerned with the air pollution monitoring taking place around energy developments in the western United States. A similar program in the midwest and eastern United States is now under development.

Audits of continuous monitors for NO_2 operated by control agencies of these states is an important part of the energy quality assurance program. Each calendar quarter an audit team visits each monitoring site and performs an audit as described above. The slope of the regression of analyzer response on audit concentrations is then used to measure performance. Figure 1 shows the impact of the quality assurance program on the quality of the data generated by the participation groups. This figure is a plot of the average difference between the slopes and unity (in terms of percentages) for each agency vs the calendar quarter when the audit was conducted. The figures in parentheses on the plot are the number of agencies taking part in the audit for each quarter. For the first two quarters, the observed errors were approximately 20% or higher. By the time of the fifth quarterly audit, the average error was below 10% and had been stable at this level for the last three audits. This improvement in performance, as demonstrated by these audits, undoubtedly has caused a corresponding improvement in the quality of the NO_2 monitoring data generated in these agencies.

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